

Bistability signatures in nonequilibrium charge transport through molecular quantum dots

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We investigate the transient nonequilibrium dynamics of a molecular junction biased by a finite voltage and strongly coupled to internal vibrational degrees of freedom. Using two different, numerical exact techniques, diagrammatic Monte Carlo and the multilayer multiconfiguration time-dependent Hartree method, we show that the steady state current through the junction may depend sensitively on the initial preparation of the system, thus revealing signatures of bistability. The influence of the bias voltage and the transient dynamics on the phenomenon of bistability is analyzed. Furthermore, a possible relation to the phenomenon of stochastic switching in nanoelectromechanical devices is discussed.

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Since the first realization of a single-molecule junction the field of molecular electronics has seen a rapid development [1, 2]. Experimental investigations of the conductance properties of single-molecule junctions have revealed a wealth of intriguing transport phenomena [3, 4].

Molecules can be considered as very small quantum dots. An important aspect that distinguishes them from semiconductor-based mesoscopic systems is the influence of the vibrational degrees of freedom. Due to the small size of molecules, the charging of the molecular bridge is often accompanied by a significant change of the nuclear geometry, which indicates strong coupling between electronic and vibrational degrees of freedom. It manifests itself in the current-voltage characteristics of molecular junctions [2, 5][6] and may result in current-induced heating of the molecular bridge [7] and large fluctuations [5]. Conformational changes of the geometry of the conducting molecule are possible mechanisms for switching behavior and negative differential resistance [4].

The experimental findings have stimulated great interest in the basic mechanisms of quantum transport at the molecular scale, in particular effects due to electronic-vibrational coupling. A variety of different theoretical methods have been applied to study these phenomena, including scattering theory, nonequilibrium Green's function approaches, and master equation methods (see, e. g., [2, 8] and references therein). Although much physical insight has been obtained by the application of these methods, all these approaches involve significant approximations.

To elucidate the detailed mechanisms and address the full complexity of the nonequilibrium transport problem, advanced numerical techniques that do not involve intrinsic approximation are required. Powerful

methods that have been proposed in this context are the diagrammatic Monte Carlo simulation (diagMC) approach [9], multilayer multiconfiguration time-dependent Hartree method in second quantization representation (ML-MCTDH-SQR) [10, 11] as well as standard quantum Monte Carlo and iterative path integral summation scheme [12, 13].

Here, we employ the first two methods to address two important and largely unsolved questions: (i) How is the steady state in a molecular quantum dot established starting from a specified preparation? (ii) Does the steady state depend on the initial preparation, e.g. on the initial occupation of the dot? In particular (ii), which is closely related to the phenomena of bistability and hysteresis, has been discussed controversially based on approximate methods [14–17]. On the other hand, there are a number of works in which hysteretic behavior was observed experimentally [18]. Our findings indicate that, for certain parameter regimes, a remarkable memory effect in the nonequilibrium dynamics exists, which manifests itself in different steady states for different initial preparations. We discuss the relation of this finding to earlier predictions of bistability for the model investigated in [14–16] as well as to stochastic switching observed in nanoelectromechanical systems [19–23].

In order to study vibrationally coupled electron transport in a molecular quantum dot we employ the resonant tunneling model given by the Hamiltonian [8, 24, 25],

$$H = H_D + H_{LR} + H_{ph} + H_T + H_I, \quad (1)$$

which describes a single electronic level of energy ϵ_D (we shall consider a spinless system and use units in which $\hbar = e = k_B = 1$ throughout), $H_D = \epsilon_D d^\dagger d$, coupled to two noninteracting fermionic reservoirs, $H_{LR} =$

$\sum_{\alpha,k} \epsilon_{\alpha k} a_{\alpha k}^\dagger a_{\alpha k}$, describing the left and right ($\alpha = L, R$) metallic electrodes with energy dispersion $\epsilon_{\alpha k}$, and a bosonic part, $H_{\text{ph}} = \sum_{\kappa} \omega_{\kappa} b_{\kappa}^\dagger b_{\kappa}$, which models the vibrational degrees of freedom of the molecule within the harmonic approximation employing normal modes with frequencies ω_{κ} . The fermionic environments serve as charge reservoirs, inducing a nonequilibrium current by virtue of the coupling between the leads and the molecular quantum dot

$$H_T = \sum_{\alpha,k} \left(t_{\alpha k} a_{\alpha k}^\dagger d + \text{h.c.} \right), \quad (2)$$

where $t_{\alpha k}$ denotes the dot-lead coupling strength between the k th electronic level of lead α and the molecule. Finally, electronic-vibrational coupling is described by the interaction part

$$H_I = d^\dagger d \sum_{\kappa} \lambda_{\kappa} (b_{\kappa} + b_{\kappa}^\dagger) + d^\dagger d \sum_{\kappa} \frac{\lambda_{\kappa}^2}{\omega_{\kappa}} \quad (3)$$

with coupling constants λ_{κ} . The last term is a counter term that corresponds to the polaron shift $\sum_{\kappa} \lambda_{\kappa}^2 / \omega_{\kappa}$. The molecule-lead and electron-vibrational couplings are characterized by the hybridization $\Gamma_{\alpha}(\epsilon) = 2\pi \sum_k |t_{\alpha k}|^2 \delta(\epsilon - \epsilon_{\alpha k})$ and spectral density $J(\omega) = \pi \sum_{\kappa} \lambda_{\kappa}^2 \delta(\omega - \omega_{\kappa})$, respectively. In our numerical studies we use different models for the molecule-lead coupling; on the qualitative level the phenomena we observe are universal and independent of them.

To characterize the nonequilibrium dynamics of the quantum dot, we consider the dot population, $P(t) = \langle d^\dagger(t) d(t) \rangle = \text{tr}\{\rho_0 d^\dagger(t) d(t)\}$, and the electrical current through the dot, $I(t) = (1/2)(d/dt)\langle N_L(t) - N_R(t) \rangle = [I_L(t) - I_R(t)]/2$. Thereby, $N_{\alpha} = \sum_k a_{\alpha k}^\dagger a_{\alpha k}$ measures the number of particles in contact α , $I_{\alpha}(t)$ are the currents from the individual electrodes to the dot, and the initial preparation is given by the density operator ρ_0 at time $t = 0$, which describes a factorizing initial state, with the dot being either empty or occupied. Initially the leads are in thermal equilibrium with energies shifted according to the chemical potentials μ_{α} ; alternatively, one could keep each of the leads filled up to different chemical potentials. In the wide band limit, the stationary currents from these two initial conditions have negligible numerical differences [26]. The bias $V = \mu_L - \mu_R$ ensures that for sufficiently long times a stationary state is reached not only for the average current $I(t)$, but also for the currents from the individual electrodes to the dot $I_{\alpha}(t)$, which are equal in the limit $t \rightarrow \infty$ [31]. In practice $I(t)$ converges to the steady state value much faster than $I_{\alpha}(t)$ though, see Fig. 1 and [9, 10].

The reached stationary nonequilibrium state is, if ergodicity holds, supposed to be unique and independent of the initial preparation of the system. Therefore, even though different preparations might yield different transient dynamics, in the long-time limit one expects to find

the transport properties independent of the evolution history. In this Letter we investigate the validity of this conjecture.

We employ two different numerical approaches, the ML-MCTDH-SQR method and the diagMC approach (see [9, 10] for details). Briefly, the ML-MCTDH-SQR method is a variational basis-set approach to study quantum dynamics for large systems containing identical particles. Within this approach the wave function is represented by a recursive, layered expansion in Fock space employing the occupation number basis. Its time evolution is then determined from the Dirac-Frenkel variational principle by dynamically optimizing all the parameters. On the other hand, the diagMC method relies on an expansion of the time evolution in terms of the dot-lead coupling. After integrating out all environmental degrees of freedom, one obtains an infinite sum over Feynman diagrams which is then evaluated by a stochastic MC scheme. Both approaches are *numerically exact*, as the respective errors can be made arbitrarily small: for diagMC, the statistical error due to the MC sampling can be easily minimized by increasing the number of MC measurements, while ML-MCTDH-SQR results can be systematically converged by increasing the number of states as well as the basis set. Both approaches yield consistent results for the transient dynamics as well as for the stationary state. Fig. 1 depicts results of both approaches for the time-dependent current for a model with a semielliptic molecule-lead coupling and an Ohmic spectral density, showing excellent agreement.

While the results of Fig. 1, corresponding to off-resonant transport, are an example for a stationary state that is independent of the initial preparation, various claims have been made regarding the existence of bistability or hysteresis in the model under investigation [14–16, 27]. These claims, however, received considerable criticism; the notion of bistable regimes in this model is anything but generally accepted [28]. Usually, the reasoning in favor of such effects assumes the existence of a parameter regime (typically requiring strong electron-phonon coupling) within which the effective potential of the phonon mode becomes multistable even in the stationary regime. Accordingly, upon entering this regime from the smaller or larger voltage domain, the system ends up in different potential minima, resulting in different stationary states and corresponding different transport properties for otherwise identical parameters [14].

These claims have been debated for almost a decade without reaching an accepted conclusion. On the one side, a general proof of non-existence of bistability is hard to give, while on the other side all previous works in favor of the phenomenon rely on approximative methods (e. g. the Born-Oppenheimer approximation of [14]) whose accuracy is difficult to judge. With our numerically exact approaches at hand, however, we can give a more detailed account of the underlying dynamics in the

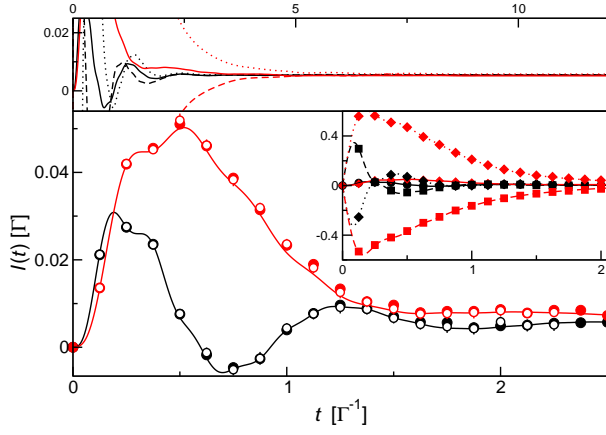


FIG. 1: (color online) Comparison of ML-MCTDH-SQR (lines) and diagMC data (symbols) for an initially empty (black) and occupied (red/grey) dot for $I(t)$ (circles/solid lines), $I_L(t)$ (squares/dashed lines), and $-I_R(t)$ (diamonds/dotted lines). The main graph shows the average current for $\epsilon_D = 4.7\Gamma$, $V = 1.25\Gamma$, $\Gamma_\alpha(\epsilon) = \Gamma\sqrt{1 - (\epsilon/\epsilon_c)^2}$ for $|\epsilon| \leq \epsilon_c$ with bandwidth $2\epsilon_c = 50\Gamma$ (semielliptic band), and an Ohmic spectral density $J(\omega) = 2\pi\omega \exp(-\omega/\omega_c)$ with $\omega_c = 0.775\Gamma$ at zero temperature; filled and open symbols refer to $I(t)$ and $[I_L(t) - I_R(t)]/2$, respectively. The inset displays the different timescales on which $I(t)$, $I_L(t)$, and $I_R(t)$ reach the stationary regime, while the upper panel demonstrates that all currents converge to the same stationary value.

proposed regimes of bistability. According to [14] the two points in parameter space which minimize the action and result in two different values for the current correspond to a nearly empty and a nearly fully occupied dot. Thus, numerical simulations with initial occupation numbers 0 and 1 should lead to the different dot configurations required for bistability to occur. Therefore, in the following we investigate the influence of the initial preparation on the stationary state, which, in the absence of bistability, should not exist. Since, as noted above, in the longtime limit all currents $I_\alpha(t)$, $I(t)$ converge to the same value, here we restrict ourselves to the stationary behavior of $I(t)$.

We consider a model with a single, strongly-coupled vibrational mode, $J(\omega) = \pi\lambda_0^2\delta(\omega - \omega_0)$. Fig. 2 shows the time-dependent current for the two different initial preparations (i.e. empty and occupied dot) at different voltages for parameters in the nonadiabatic regime, i. e. $\omega_0 > \Gamma$. Strikingly, the currents converge towards stationary values on timescales roughly of the order of Γ^{-1} for almost all voltages. This is in accordance with many previous studies of the real-time dynamics, both for the present [29] as well as for the Anderson model [26] and can be rationalized by noting that the strength of the tunneling coupling Γ defines the typical timescale for charge dynamics. However, except for the high voltages the stationary values of the current are clearly different, with

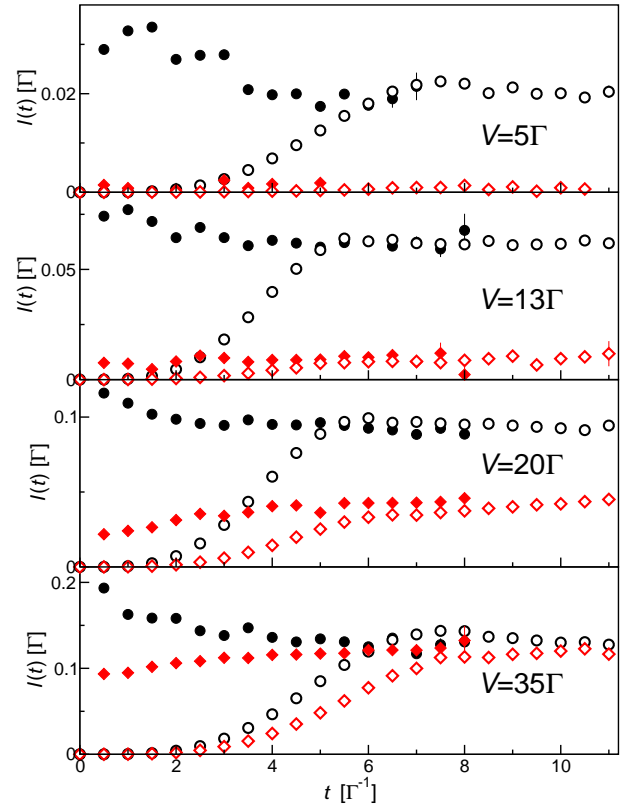


FIG. 2: Current $I(t)$ for $\epsilon_D = -5\Gamma$, $\Gamma_\alpha(\epsilon) = \Gamma/2$ for $|\epsilon| \leq \epsilon_c$ (flat band), and a single phonon mode with $\lambda_0 = 8\Gamma$ and $\omega_0 = 4\Gamma$, for an initially empty (black) and occupied (red) dot at zero temperature. Open symbols refer to diagMC data for a smooth switch-on of the tunneling coupling, $\Gamma(\epsilon, t) = \sin^2[\pi t/(2\tau_{\text{sw}})]\Gamma(\epsilon)$ for $t \leq \tau_{\text{sw}}$ ($= 8\Gamma^{-1}$ for $V = 5\Gamma$ and 35Γ , else $6\Gamma^{-1}$), while filled symbols refer to an instantaneous switch-on. The bandwidth is $2\epsilon_c = 41\Gamma$ for $V = 35\Gamma$, else 26Γ .

the initially empty dot leading to a significantly larger current than the initially occupied one. This intriguing finding contradicts the notion of an unique stationary state and instead supports the idea of bistability. A similar result is obtained in the adiabatic regime of rather slow vibrational motion, i.e. $\omega_0 < \Gamma$, depicted in Fig. 3. This is the regime originally suggested for the existence of bistability in the theoretical approaches [14]. The numerical results in Figs. 2, 3 indicate the dependence of the long-time current on the initial occupation of the dot. This finding is corroborated by the dynamics of the population of the dot (data not shown). The population of the dot may converge to its stationary value on a significantly longer timescale than the current. However, for the examples considered above its stationary state exhibits a dependence on the initial occupation even more pronounced than for the current.

The comparison of the different panels in Fig. 2 shows that the sensitivity of the dependence of the current on

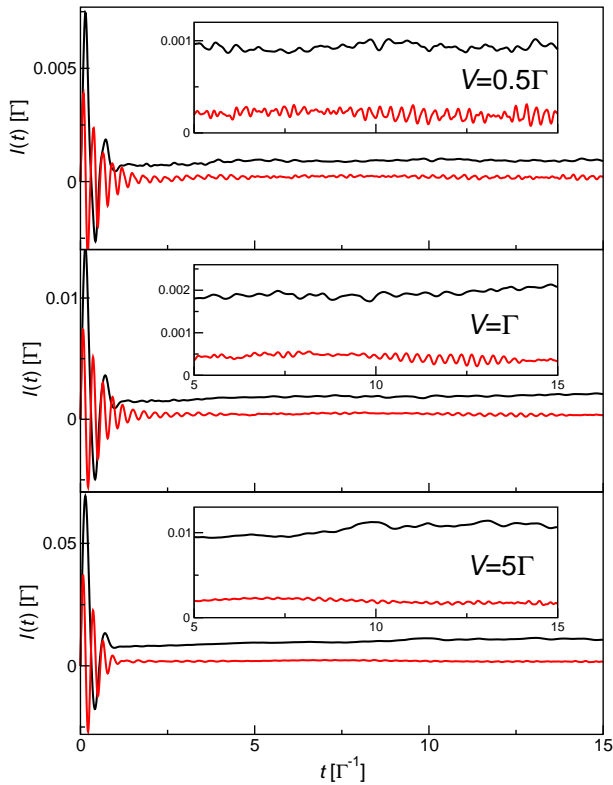


FIG. 3: Similar to Fig. 2 but with ML-MCTDH-SQR result for the parameters: $\epsilon_D = -2.5\Gamma$, $\omega_0 = \Gamma/8$, $\lambda_0 = \Gamma$, and a bandwidth $2\epsilon_c = 20\Gamma$. *Insets*: Magnified versions of the same plots in the stationary regime.

the initial preparation is influenced by the applied bias voltage. While for $V = 35\Gamma$ both currents are approaching each other within a timescale τ_{st} of the order of Γ^{-1} they still seem to be transient for $V = 20\Gamma$ within the times accessible by our simulations. Here, it is not clear whether both currents converge to different or the same stationary value. In the latter case the corresponding stationary timescale τ_{st} would be much larger than Γ^{-1} , offering an alternative explanation for the mismatch in the current for not too large voltages in both, Figs. 2 and 3. Instead of identifying the plateau value as the actual steady state, it could be interpreted as a transient current with a timescale τ_{st} exceeding Γ^{-1} by orders of magnitude.

The temperature T of the leads has a similar influence on the effect: an increase of T destroys the bistability signatures just as an increase of V does. On the other hand, it is noted that the difference in the long-time behavior is independent of the details of the initial switch-on of the tunneling coupling (cf. Fig. 2) as well as of the specific form of the hybridization (i.e. semielliptic vs. flat band).

We would like to stress that the numerically exact, time-dependent methods employed in our studies cannot directly address the stationary state, which is formally

obtained in the infinite time limit, but only map the dynamics over long but finite timescales. It is thus not possible to unambiguously determine whether the differences in the long-time transport behavior account for truly distinct stationary states, or whether the corresponding transport properties would still decay to the same unique stationary value, void of any imprints of the preparation, on timescales significantly longer than those covered by our calculations. While in the latter case the concept of bistability does not have to be introduced, an explanation for this surprisingly strong separation of timescales is, to our knowledge, still lacking – that is, the timescales necessary to reach the true stationary state within and outside the aforementioned parameter regime.

Since the pronounced transient dynamics always die out on the same timescale (of the order of Γ^{-1}), we conclude that the effect is not *caused* but merely *triggered* by the changes in the initial preparations. Furthermore, the phenomenon seems to be completely unaffected by details of the transient dynamics. For voltages at which we observe the separation of timescales, the current originating from an instantaneous initial switch-on of the tunneling coupling exhibits very rich transient dynamics, suggesting a rather extensive exploration of the effective potential surfaces, while for a continuous switch-on process, one finds quite a smooth convergence process. Yet in both cases we observe the same separation of timescales. Since the system lacks any energy scale which can be set in relation to this novel long timescale it should, if finite, be generated in a yet unknown way.

We also would like to mention that the described phenomenon is not directly related to the stochastic switching processes leading among other things to random telegraph noise frequently discussed in the context of shuttling in nanoelectromechanical devices [19–23]. While the switching times would be of the order of $10^3 - 10^4$ in units of Γ^{-1} for most of the plots shown above (we use the procedure from [21]) and thus apparently in accordance with the reported data, we would like to point out that our simulations would then describe the very *onset* of the stochastic switching process, which is not covered by any of the existing studies.

We finally comment on the applicability of our findings, obtained for the standard model of vibrationally-coupled electron transport, to realistic molecular junctions. Typical values of the coupling Γ vary between meV and a few eV, depending on the specifics of the binding group and the geometry. Assuming an average value of $\Gamma = 0.1$ eV (which is realized, e. g. in benzenealkenethiol-gold junctions [30]), our results predict the phenomenon of bistability to occur both in the nonadiabatic regime (e. g. for a vibrational mode with a higher frequency of $\omega_0 = 0.4$ eV as in Fig. 2) as well as in the adiabatic regime (e. g. $\omega_0 = 0.0125$ eV as in Fig. 3) for sufficiently large electronic vibrational coupling ($\lambda/\omega_0 \gtrsim 1$) and not too large voltages ($V < 2$ V). These parameters are expected to be

of relevance for many molecular junctions, e.g. for some of the molecular junctions, where hysteretic behavior was observed experimentally [18]. According to our results, the phenomenon of bistability persists on a timescale of at least a picosecond, which is longer than typical vibrational periods. It should be observable with methods of femtosecond spectroscopy. In view of the current experimental progress [7], spectroscopic techniques that allow to directly monitor ultrafast processes in molecular junctions are expected to become available in the near future.

To summarize, we have presented numerically exact results for the nonequilibrium dynamics of a molecular quantum dot. In a wide parameter range we find a distinct dependence of the steady state current on the initial preparation of the molecular junction. Our analysis shows that this phenomenon is related to the previously predicted bistability of the model. In contrast to the previous approximate approaches, the present numerically exact results unambiguously prove the existence of bistability signatures in the dynamics over a time scale significantly longer than the tunneling time.

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